

# Study of thorium association and surface precipitation on colloids

C. Degueldre <sup>a,\*</sup>, A. Kline <sup>b</sup>

<sup>a</sup> Nuclear and safety division, Paul Scherrer Institute, 5232 Villigen, Switzerland

<sup>b</sup> University of Missouri, Columbia, Missouri USA

Received 10 April 2007; received in revised form 20 August 2007; accepted 11 September 2007

Available online 22 September 2007

Editor: R.W. Carlson

## Abstract

Thorium is known to sorb strongly on environmental particles, however, its sorption coefficient need to be formally quantified to justify its use as a tracer or to study his behaviour on environmental particles. A surface complexation model was developed to simulate metal sorption on colloids and precipitation by polymerization at their surface. Correlations between hydrolysis and surface complexation are systematically used to estimate all surface complexation constants on the basis of the corresponding hydrolysis constant. The model is based on the metal adsorption on free sites as well as on already contaminated sites. The distribution coefficient ( $K_d$ ) is calculated for the Th(IV) sorption and polymerization onto  $Al_2O_3$ ,  $TiO_2$ ,  $FeOOH$ , and  $SiO_2$  colloids. The calculations were performed for the effect of various polymer chain lengths, pH, the radius of the colloids, and the concentration of both the metal and colloid. It was verified that the highest sorption occurs at approximately neutral pH values. It is shown that at low metal concentrations, polymerization does not significantly affect the distribution coefficient, but as the metal concentrations reaches the concentration of the surface sites, the distribution coefficients could increase before tapering off at saturation for limited polymer sizes. As the size of the colloid particles decreases the distribution coefficients increase as expected for a given mass concentration. When comparing the effect of colloid material,  $TiO_2$  displays the highest  $K_d$  values followed by  $Al_2O_3$ ,  $FeOOH$ , and finally  $SiO_2$ . Since the polymerization is an effect of the metal and not of the type of colloid, once the polymerization begins affecting the  $K_d$ , the values for all four types of the colloids would become similar. However, thorium saturation in the solution apparently occurs prior to polymerization. The  $K_d$  values gained from the literature are comparable with those calculated using the presented model.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** colloids; thorium; surface complexation; polymerization

## 1. Introduction

Since more than 50 yr (e.g. Holland & Kulp, 1954), thorium isotopes occupy a special place in the environment scientist toolbox as tracers for studying the behaviour of particles and their fluxes in shallow waters (Aellen et al., 1993), rivers (El-Gamal et al., 2007;

Dosseto et al., 2006; Corbett et al., 2004; Martínez-Aguirre et al., 1995), lakes (Dominik et al., 1989), estuaries (Lei Zhang et al., 2004; Feng et al., 1999), seas (Santschi et al., 2006; Roy-Barman et al., 2002) or oceans (Coppola et al., 2006; Trimble et al., 2004). Due to their constant production rates from soluble parent nuclides of uranium and radium, their disequilibrium can be used to calculate rates and time scales of sinking particles. In addition, by ratioing particulate  $^{234}Th$  as well, in principle, other Th-nuclides in the water column, it is possible to calculate fluxes elements associated to the particles. Most

\* Corresponding author. Tel.: +41 56 3104176.

E-mail address: [claudedegueldre@psi.ch](mailto:claudedegueldre@psi.ch) (C. Degueldre).

of these applications are possible with little knowledge of the chemical properties of thorium, other than its oxidation state (IV) and tendency to strongly sorb to surfaces. However the sorption process has to be quantified.

Among the thorium natural radioisotope,  $^{232}\text{Th}$  which is present at higher concentration than its tracer isotopes is also studied (e.g. El-Gamal et al., 2007). In the environmental systems the behaviour of  $^{232}\text{Th}$  in water is affected by colloidal particles, which form as a result of water–rock interaction, input of erosion from rivers or/and local biogenic activity (e.g. McCarthy & Degueldre, 1993). In subsurface systems, the Th (or other tetravalent actinides) contaminated colloids may migrate through the aquifer and travel further distances than expected using a 2 phase model such as described earlier (Nagasaki et al., 1997; Smith & Degueldre, 1993).

For thorium in aqueous phases, pH plays an important role due to the hydrolyzation of the species that each have different sorption tendencies (Baes & Mesmer, 1976; Johnson & Toth, 1978). There has also been evidence that thorium may form polymer chains attaching on the colloid particle instead of only sorbing at the host rock surface site e.g. (Lieser, 1995). These polymer chains may increase the amount of metal that may be associated to the colloid, therefore transporting higher quantities outside of the source by increasing its sorption coefficient  $K_d$ .

The purpose of this study is to examine the association of a metal ion such as thorium and the construction of its polymers on colloids and apply the calculations. The model was developed to calculate the distribution coefficient for different polymer chain lengths. In this work, the effects of pH, colloid radius, type of colloid, and Th concentration and colloid particles are investigated and compared with the  $K_d$  data found in the literature.

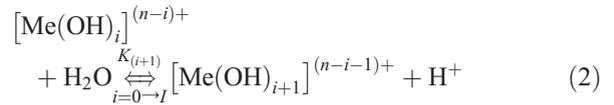
## 2. Theoretical background

The association of the metal (Me) on the colloid is treated as a reversible sorption of the metal on a single active group (>SOH) with a surface complexation mechanism. In these conditions a distribution coefficient ( $K_d$ ) defines the amount of metal ion that sorbs onto the colloid particles. At equilibrium, the distribution coefficient is defined by:

$$K_d = \frac{[\text{Me}]_{\text{sorb}}}{[\text{Me}]_{\text{soln}}[\text{coll}]} \quad (1)$$

where [Me] is the concentration of the metal either on the colloid (sorb) or in solution (soln). Its use limitation for retardation studies must be clearly restricted to equilibrium (McKinley & Alexander, 1993).

Due to the aqueous solution and the metal being a cation, hydrolysis must be taken into account. The stepwise hydrolysis reaction is described by:



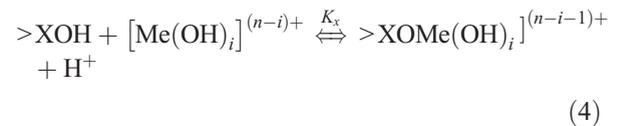
where  $n$  is the charge of the non-hydrolyzed metal ion and  $K_{(i+1)}$  is:

$$K_{(i+1)} = \frac{[\text{Me}(\text{OH})_{i+1}]^{(n-i-1)+} [\text{H}^+]}{[\text{Me}(\text{OH})_i]^{(n-i)+}} \quad (3)$$

The metal in solution is supposed to form mononuclear complexes only (without soluble polymers), and the solution is treated as under- or over-saturated (without precipitation).

Protonation or deprotonation may also occur on the surface sites >SOH of the colloid particles with S is the cation of the substrate.

The following equation generalizes sorption on a site >XOH, where X is either S (substrate cation) or Me (sorbed metal), according to the reaction:



where the surface complexation constant,  $K_x$ , is equal to:

$$K_x = \frac{[>\text{XOMe}(\text{OH})_i]^{(n-i-1)+} [\text{H}^+]}{[>\text{XOH}] [\text{Me}(\text{OH})_i]^{(n-i)+}} \quad (5)$$

Sorption of the site >SOH is defined by a surface complexation constant,  $K_s$ , on the naked site, and  $K_p$  on the already contaminated site. Correlations between  $K_x$  and  $K_i$  such as those reported for the respective cumulative constants (Stumm, 1987) can be used to calculate the  $K_s$  values (Degueldre et al., 1994; Degueldre, 1995; Alonso & Degueldre, 2003).

In sorption there are 4 cases that can occur. In the first case there is no polymerization occurring and therefore  $K_p$  is essentially 0. In the second case  $K_s$  is larger than  $K_p$  and the colloid's surface will become covered before polymerization begins. In the third case  $K_p$  and  $K_s$  are equivalent, in which there is an equal affinity for both initial attachment and polymerization. The fourth case is when  $K_p$  is larger than  $K_s$ , in this situation once a metal has attached to the colloid there is a higher affinity for a

second metal ion to form the polymer chain than to fill a vacant surface site.

In the case of  $K_p \lll K_s$  without polymerization, the reaction of the metal with the surface site occurs on a  $>SOH$  site.  $K_{s(0,i+1)}$  represents that the metal is attaching to the naked surface site.

For the case with polyvalent metals the metal concentration in solution is:

$$[Me]_{\text{soln}} = [Me^{n+}] \frac{1}{\xi_{\text{soln}}} \quad (6)$$

where the distribution function,  $\xi_{\text{soln}}$ , is defined as:

$$\frac{1}{\xi_{\text{soln}}} = 1 + \sum_{i=1}^I \left( \frac{\prod_{i=1}^I K_i}{[H^+]^i} \right) \quad (7)$$

The metal in solution is supposed to form mononuclear complexes only, and the solution is under- or over-saturated. The concentration of the metal that is sorbed is:

$$[Me]_{\text{sorb}} = \frac{[Me^{n+}][>SOH]}{[H^+]} \left( \frac{1}{\xi_{\text{sorb}}} \right) \quad (8)$$

where  $\xi_{\text{sorb}}$  is equal to:

$$\frac{1}{\xi_{\text{sorb}}} = K_{s(0,1)} + \sum_{i=1}^I \left( \frac{K_{s(0,i+1)} \prod_{i=1}^I K_i}{[H^+]^i} \right) \quad (9)$$

Since neither  $[Me^{n+}]$  or  $[>SOH]$  are known, Eqs. (6) and (10) are set up for to solve for them as a system of 2 equations and 2 unknowns. The total site concentration is then:

$$[>SOH]_{\text{tot}} = [>SOH] \left( \frac{1}{\xi_{>SOH}} + \frac{[Me^{n+}]}{[H^+]} \left\{ \frac{1}{\xi_{\text{sorb}}} \right\} \right) \quad (10)$$

where  $\xi_{>SOH}$  is given by:

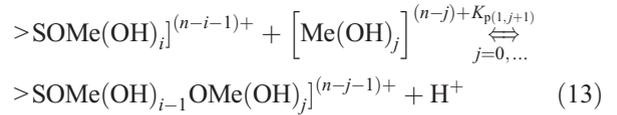
$$\frac{1}{\xi_{>SOH}} = 1 + K_{a1}[H^+] + \frac{1}{K_{a2}[H^+]} \quad (11)$$

and Eq.(6) can be obtained by substitution for the total metal concentration. Substituting these equations into Eq. (1) gives the final distribution coefficient:

$$K_d = \frac{[>SOH]}{[H^+][\text{coll}]} \left( \frac{\xi_{\text{soln}}}{\xi_{\text{sorb}}} \right) \quad (12)$$

In the cases of  $K_p > K_s$ ,  $K_p = K_s$ ,  $K_p < K_s$ , with significant polymerization, the sorption of the next free

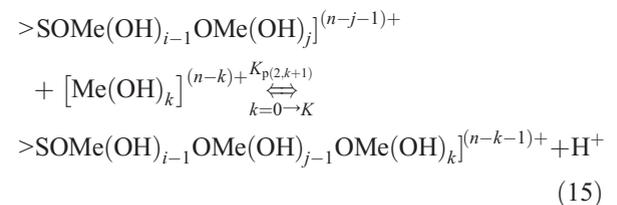
metal ion has an affinity to bind with the metal ion that is already attached to the colloid, a polymer chain will form:



where  $K_{p(1,j+1)}$ , on which 1 denotes the sorption on the first metal loaded site, and  $j$  represents the hydroxyl complex forming, is equal to:

$$K_{p(1,j+1)} = \frac{[>SOMe(OH)_{i-1}OMe(OH)_j]^{(n-j-1)+} [H^+]}{[>SOMe(OH)_i]^{(n-i-1)+} [Me(OH)_j]^{(n-j)+}} \quad (14)$$

The next attachment of a free metal ion would be:



where  $K_{p(2,k+1)}$  is equal to:

$$K_{p(2,k+1)} = \frac{[>SOMe(OH)_{i-1}OMe(OH)_{j-1}OMe(OH)_k]^{(n-k-1)+} [H^+]}{[>SOMe(OH)_{i-1}OMe(OH)_j]^{(n-j-1)+} [Me(OH)_k]^{(n-k)+}} \quad (16)$$

and this will continue as long as the polymer chain lengthens. In this model it is assumed that a single free metal ion has a higher affinity to sorb onto an already sorbed metal ion at the end of the polymer chain, than it would to sorb onto a metal ion in the middle of the polymer chain. In the tetravalent metal ion case, multiple branches could form off of the  $>Me(OH)_2^{(n-2)+}$ ,  $>Me(OH)_3^{(n-3)+}$ , and  $>Me(OH)_4^{(n-4)+}$  that were in the middle of the polymer chain due to the multiple OH groups. It may be demonstrated by correlation that this reaction is less favorable for branching than for linear polymer formation from a free energy point of view.

As a simplification, it was assumed that the  $K_{s(i,j)}$  values for each  $i$  greater than zero were approximately the same. The total concentration of the metal in solution will be the same as in Eq. (6), unless it is taken into account

that polymers may form in solution without the colloid particle. The concentration of the metal on the colloid will be different however as shown in the equation:

$$[\text{Me}]_{\text{sorb}} = \frac{[>\text{SOH}][\text{Me}^{n+}]}{[\text{H}^+]} \left( \frac{1}{\xi_{\text{sorb}}} \right) + [>\text{SOH}] \left( \frac{1}{\xi_{\text{sorb}}} - K_{\text{s}(0,1)} \right) \left( \frac{1}{\xi_{\text{poly}}} \right) \times \left( \frac{[\text{Me}^{n+}]}{[\text{H}^+]} \right)^2 (2 + 3\mathcal{R} + 4\mathcal{R}^2 + \dots (\pi)\mathcal{R}^{\pi-2}) \quad (17)$$

where  $p$  is the number of links in the polymer chain,  $\xi_{\text{poly}}$  is:

$$\frac{1}{\xi_{\text{poly}}} = K_{\text{p}(0,1)} + \sum_{i=1}^l \left( \frac{K_{\text{p}(0,i+1)} \prod_{i=1}^l K_i}{[\text{H}^+]^i} \right) \quad (18)$$

$\mathcal{R}$  is:

$$\mathcal{R} = \left( \frac{1}{\xi_{\text{poly}}} - K_{\text{p}(0,1)} \right) \frac{[\text{Me}^{n+}]}{[\text{H}^+]} \quad (19)$$

and  $K_{\text{p}(i,j)}$  is the polymerization coefficient. In Eqs. (17) and (19) the subtraction of the  $K_{\text{s}(0,1)}$  and  $K_{\text{p}(0,1)}$  values correct for the inability of the naked ion to give up a proton and therefore allow further attachments. The total metal concentration can then be solved for using Eq. (6). The total site concentration is:

$$[>\text{SOH}]_{\text{tot}} = [>\text{SOH}] \frac{1}{\xi_{>\text{SOH}}} + \sum_{j=1}^J \sum_{i=0}^l \left[ >\text{S}(\text{OMe}(\text{OH})_{i-1})_j \right]^{(n-j-1)+} \quad (20)$$

This equation and Eq. (17), substituted into Eq. (6), are used to solve for the  $[>\text{SOH}]$  and  $[\text{Me}^{n+}]$  as before in Section 2. Finally, the distribution coefficient is calculated:

$$K_d = \frac{\xi_{\text{soln}} [>\text{SOH}]}{[\text{H}^+][\text{coll}]} \left( \frac{1}{\xi_{\text{sorb}}} + \left( \frac{1}{\xi_{\text{poly}}} \right) \left( \frac{1}{\xi_{\text{sorb}}} - K_{\text{s}(0,1)} \right) \frac{[\text{Me}^{n+}]}{[\text{H}^+]} \times \left\{ 2 + 3\mathcal{R} + 4\mathcal{R}^2 + \dots + (\pi)\mathcal{R}^{\pi-2} \right\} \right) \quad (21)$$

where again  $\pi$  is the length of the polymer chain. For all of the cases in which the polymerization coefficient does

not equal zero, this same set of equations is used. The differences will emerge when the  $K_p$  values are inserted into the equations.

### 3. Results

Calculations for the surface complexation without polymerization calculations were performed using EXCEL while Mathematica was used for polymerization (to solve the higher order polynomial equations) and EXCEL for the other compilations.

The distribution of hydrolyzed thorium can be calculated using the intrinsic thermodynamic data presented in Table 1 (correction could be done for high ionic strengths  $I$ ). Around a neutral pH tri- and tetra-hydroxyl complexes may be formed in significant quantities. In this study, thorium is considered to be under- and over-saturated and without soluble thorium polymer, however polymer formation and solubility data are known (Neck et al., 2002) and compared to the sorption/surface precipitation results. The data in Table 2 shows the correlations used for the surface complexation constants,  $K_x$  evaluation, and the  $\text{p}K_a$  values used for the colloid surface sites. The calculation of distribution of the ternary surface complexes onto the  $\text{Al}_2\text{O}_3$  colloid surface for a dilute thorium solution shows that at approximately neutral solutions the major species are:  $>\text{AlOTh}(\text{OH})_i]^{(n-i-1)+}$  when  $i$  is equal to 2 or 3.

In order to estimate the polymerization constants for the free ion attaching to the polymer chain it was desired that the attachment of these ions have a slightly higher affinity than for that of the surface site. Using the relation of  $K_{X_i}$  to  $K_i$  given in Table 2, it was reasoned that the relation of the surface complexation constants for  $\text{TiO}_2$  would be used as an estimation for an analogue of  $\text{ThO}_2$ , since they were stronger than that of  $\text{Al}_2\text{O}_3$ . When polymerization was taken into account as shown in Fig. 1, there was no effect on the distribution coefficient at low concentrations of thorium. However, as concentration was increased there was a rise in the distribution coefficient in the region where the site concentration was equal to the thorium concentration.

Table 1  
Hydrolysis constants ( $I=0$ ) for thorium (Neck et al., 2002)

Species	$i$	$\log(K_i)$
$\text{Th}^{4+}$	1	-2.2
$\text{Th}(\text{OH})^{3+}$	2	-3.8
$\text{Th}(\text{OH})_2^{2+}$	3	-5.0
$\text{Th}(\text{OH})_3^+$	4	-6.5
$\text{Th}(\text{OH})_4$	5	-15 <sup>a</sup>

<sup>a</sup> Best estimation of value required for calculations.

Table 2

Surface complexation correlations by decreasing energy for  $\text{TiO}_2$  (James and Healy, 1972), for  $\text{Al}_2\text{O}_3$  (Hachiya et al., 1984), for  $\text{FeOOH}$  (Balistieri et al., 1981) and for  $\text{SiO}_2$  (Righetto et al., 1991) and site  $\text{p}K_a$  e.g. (Stumm, 1987)

	$\text{TiO}_2$	$\text{Al}_2\text{O}_3$	$\text{FeOOH}$	$\text{SiO}_2$
$\text{Log}(K_{X_i})$	$6.57 + 1.04 \log(K_i)$	$6.02 + 0.98 \log(K_i)$	$3.75 + 0.75 \log(K_i)$	$2.00 + 0.65 \log(K_i)$
$\text{p}K_{a1}$	2.7	5	4	–
$\text{p}K_{a2}$	9.1	10	9–10	7

Correlation for  $\text{TiO}_2$  as an analogue of  $\text{ThO}_2$  when not stated.

Fig. 1 shows the distribution coefficient with the effect of the polymerization at varying pH values. The maximum sorption obtained at low thorium concentrations was around a pH of 8, which was slightly higher than that of pH 7. An interesting feature though was that at higher thorium concentration the solution with a pH of 6 was slightly higher than that of pH 8. The results from this graph are reasonable, because if the distribution coefficient is standardized to a value of 1 then as the polymer chain is increased by a factor of 10, the  $\log(K_d)$  value increased by 1.

The concentration of the colloid in solution also contributed to the distribution coefficient. Calculations show that there was not much of a difference between a 0.1 and a 1 ppm solution. But, as the concentration was increased above 1 ppm there was a significant increase in the distribution coefficient at the larger thorium concentrations. However, a polymer chain of 5 was used as an

example, and the other polymer chain lengths displayed similar results.

The effect of the size of the colloids on sorption was also investigated for a given mass concentration. The radii of the  $\text{Al}_2\text{O}_3$  particles for 10, 100 and 1000 nm showed decreased of  $K_d$  proportional to the colloid size as expected. This trend is similar to the effect reported by Lu et al. (2003), this is due to the actinide sorbed per unit mass of colloid being higher at lower concentrations.

In the situation where affinities were equal for initial surface site attachment and actinide polymerization on the colloid, the distribution coefficient was still similar to the case where the polymerization had the higher affinity dictated by the  $\text{TiO}_2$  correlation. As seen in Fig. 2a, the distribution coefficient was only slightly lower for this case than for the higher affinity ( $\text{TiO}_2$ ) polymerization case. This was expected because in both cases the same amount of colloid was sorbed, but in the case of equal

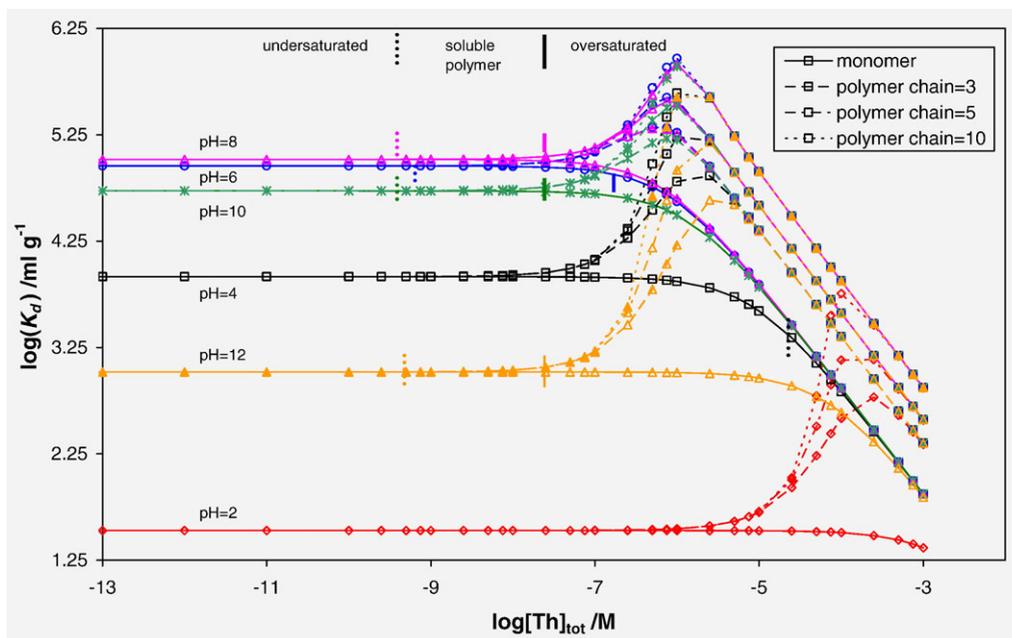


Fig. 1. Distribution coefficient as a function of total thorium concentration for different pH values Conditions: Polymer chain =  $\pi$ ,  $\text{Al}_2\text{O}_3$  colloid of radius 100 nm with  $[\text{coll}] = 10^{-6} \text{ g mL}^{-1}$  and  $[>\text{SOH}]_{\text{tot}} = 7.48 \times 10^{-8} \text{ M}$  at a pH 7. Note: With thorium under- and over-saturated and without soluble thorium polymer e.g. Bitea et al. (2003).

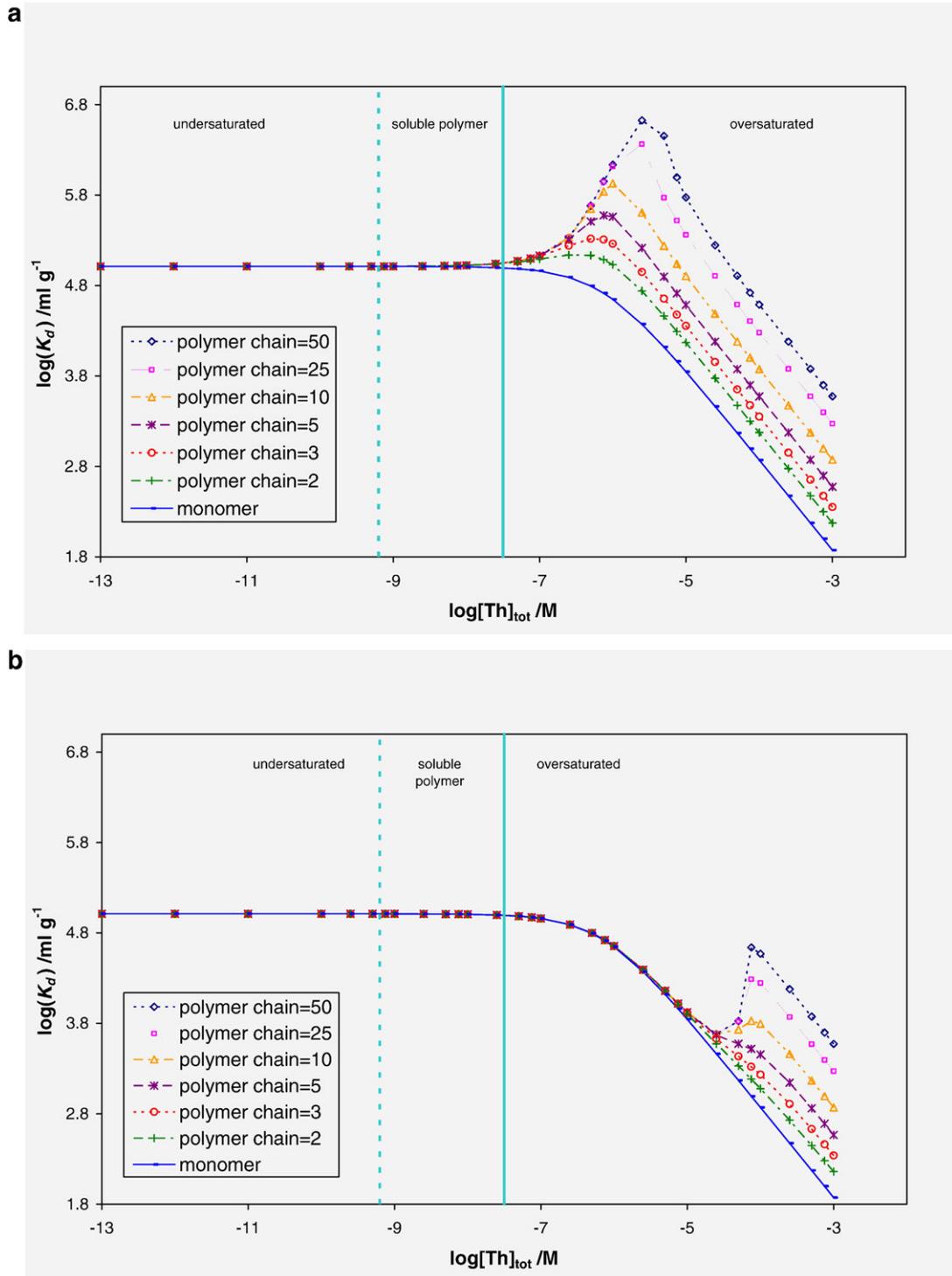


Fig. 2. Distribution coefficient as a function of thorium concentration for various polymer chain  $=\pi$ . a.  $K_s > K_p$  with correlations  $>\text{AlOH}$  and  $>\text{TiOH}$  b.  $K_s > K_p$ , with correlations  $>\text{AlOH}$  and  $>\text{SiOH}$  respectively. Conditions:  $\text{Al}_2\text{O}_3$  colloids of radius 100 nm with  $[\text{coll}] = 10^{-6} \text{ g mL}^{-1}$  and  $[>\text{SOH}]_{\text{tot}} = 7.48 \times 10^{-8} \text{ M}$  at a pH 7 and where polymer chain  $=\pi$ . Note: With thorium under- and over-saturated and without soluble thorium polymer.

affinities the polymerization affinity was less than that in the other case, resulting in the metal to be sorbed with less strength.

For the remaining case it was investigated when  $K_p$  is smaller than  $K_s$ . In this case the metal will coat the colloid first and may subsequently begin to form polymer chains after the initial layer is completely formed. The correlations shown in Table 2 were used to construct Fig. 2b. For the correlation of the polymerization the data from  $\text{SiO}_2$  was used, because it was lower than that of  $\text{Al}_2\text{O}_3$ . As seen in Fig. 2b, the distribution coefficient is equal to that of the single layer until high enough concentrations of metal are obtained that the polymers are able to form, and at this concentration and over the distribution coefficients significantly increase.

The type of colloid was the final parameter investigated for the sorption of thorium. The correlations in Table 2 were used to determine the surface complexation constants of  $\text{TiO}_2$ ,  $\text{FeOOH}$ , and  $\text{SiO}_2$  colloid particles. The polymerization constant remained the same as before, because it was assumed that once the initial surface attachment of the metal took place the affinity for the polymer chain was not dependent upon the colloid particle. As shown in Fig. 3, out of the 4 colloid types evaluated  $\text{TiO}_2$  had the highest distribution coefficient followed by  $\text{Al}_2\text{O}_3$  then  $\text{FeOOH}$  and finally  $\text{SiO}_2$ . In this figure after a certain thorium concentration the polymer chains of similar lengths had comparable distribution coefficient, as expected. This trend is a result of the same

polymerization constants being used for each type of colloid particle; therefore even though  $\text{SiO}_2$  has a lower distribution coefficient at lower concentrations of the metal, due to the polymerization it will have the same distribution coefficient at higher concentrations of metal. In all of these cases the developed model in this study supposes that the thorium remains soluble as hydroxo mononuclear complexes in solution without formation of soluble polymer while the solution being under- or over-saturated.

#### 4. Discussion

There have been numerous sorption studies of thorium on colloid. This reflects the importance of thorium isotopes used as natural radiotracers to study the natural environment e.g. Chase et al. (2002) or as analogue nuclide of other tetravalent actinides for simulating the environment of a radioactive waste repository as reported by Reiller et al. (2002).

Chase et al. (2002), studied the influence of particle composition and particle flux on scavenging of Th in the ocean. For opal (may be covered by  $>\text{FeOH}$ ), the partition coefficient for Th was found to be  $3.9 \times 10^5 \text{ g mL}^{-1}$ . Partition coefficients decrease with increasing particle flux in open-ocean settings, but not in an ocean-margin region.

Niven and Moore (1993), studied the thorium sorption in seawater suspensions of aluminium oxide particles in

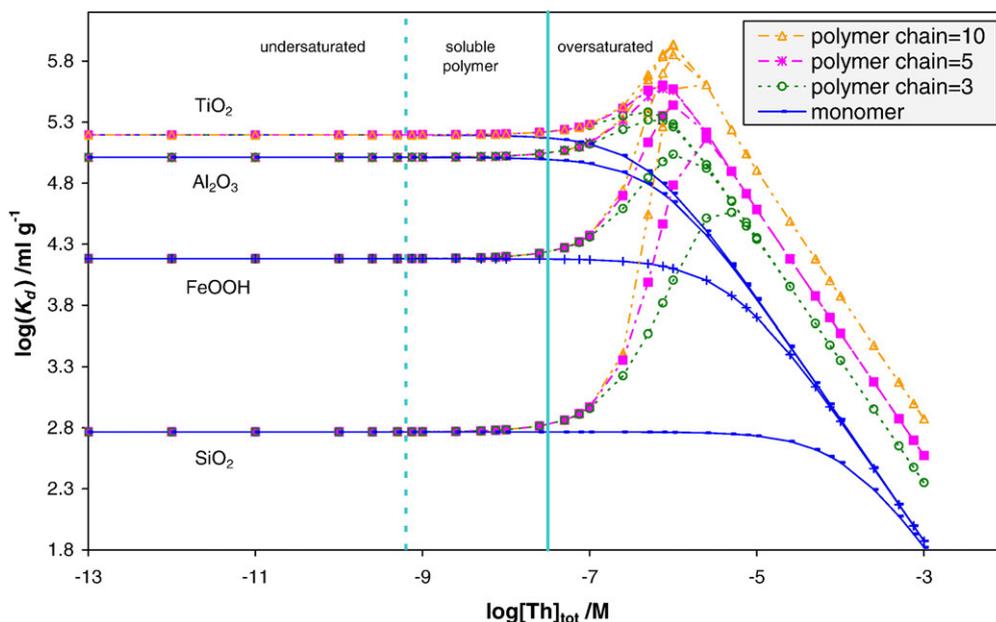


Fig. 3. Distribution coefficient for thorium onto  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{FeOOH}$ , and  $\text{SiO}_2$  where polymer chain =  $\pi$ . Conditions: Colloid of radius 100 nm with  $[\text{coll}] = 10^{-6} \text{ g mL}^{-1}$  and  $[\text{SOH}]_{\text{tot}} = 7.48 \times 10^{-8} \text{ M}$  at a pH 7. Note: With thorium under- and over-saturated and without soluble thorium polymer.

controlled laboratory experiments to determine whether partitioning is consistent with current models of trace-metal adsorption (surface complexation models). Experimental conditions (i.e., thorium and particle concentrations, pH, temperature, salinity) were chosen to be for coastal seawater while minimizing non-adsorptive processes;  $^{234}\text{Th}$  was used as a tracer of thorium. The comparison of these experimental results with the predictions by surface complexation models shows that thorium sorption in the alumina suspensions is consistent with our model (Table 3).  $K_d$  values were independent of particle concentration and salinity.

Several studies present the fraction of thorium absorbed on the colloids, they can, however, not be used in this study to test the model because the data in the graphs are difficult to be used (% sorption and not  $K_d$  values) e.g. Östhols (1995), or, Murphy et al. (1999). The most useful data are those reported by Hongxia et al. (2006) for  $\text{Al}_2\text{O}_3$ , Chen and Wang (2007a,b) for  $\text{SiO}_2$ , and, by Tan et al. (2007) and Jakobsson (1999) for  $\text{TiO}_2$ . The data presented by these authors are compared in Table 3 with the data calculated from this study. The comparison of the experimental and modeling data requires knowledge of the colloid material, colloid size, solution pH and Th concentration. For low Th concentrations and for the pH ranging from 4–5 to 10,  $\log K_d$  is rather constant. If the polymerization of Th takes place,  $K_d$  values should increase with the Th concentration. For chain including 10 Th,  $K_d$  increases by 1 order of magnitude. This effect is however not observed since precipitation takes place in water prior to polymerization onto the colloids. Generally, the batch tests are carried out in a titration mode, starting with rather low pH where Th is soluble and weakly sorbing. When the pH increases, thorium sorption becomes stronger reducing the Th concentration in water. The loading on the colloid phase increases gradually avoiding precipitation in the aqueous phase.

Östhols 1995, presents the Th sorption edge around pH 3–4 on 25 nm  $\text{SiO}_2$  colloids and shows that the sorption follows a Langmuirian isotherm at pH 3 excepted at high loading. The author notes: ‘this could

be formation of large Th cluster/polymers in solution analogous to those found for U(IV) (Hietan, 1956)’.

The nature of the colloids, or more precisely their coverage, should be a relevant parameter since the sorption affinity is a function of the element forming the active sites. Model calculations show that the sorption is stronger through the series:  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ . This effect is also shown in the experimental data presented Table 3. Another important parameter is the size of the colloids, or, the specific surface (BET). For a given colloid concentration, the sorption coefficient is proportional to the inverse of the colloid diameter or size. The model of polymer build-up shows that precipitation or polymerization may first take place in solution prior to polymerization on the colloids. These phases may then attach to the studied colloid but this mechanism is behind that studied in this study.

As noted by Li Yuan-Hui (1981), ‘The adsorption of elements on the hydrous oxide surface of iron oxide, manganese oxide and clay minerals is the most important ultimate removal mechanism of most of the elements from the ocean’. Among the elements investigated Th is one of the most sorbing. The experimental sorption ratio’s (around pH 8 for Atlantic ocean and Amazonia river water) are plotted as a function of first hydrolysis constant as calculated formally with our surface complexation model (Degueldre et al., 1994). Clearly the model developed in this work yields for Th comparable results for Amazonia river water particles e.g.  $\log K_d$  of 5.2. For ocean water particles the values are two orders of magnitude larger due to the effect of the scavenging and colloid aggregation coupling in sea water.

## 5. Conclusion

Using the modeling approach developed in this study, the thorium sorption coefficient was calculated as a function of the total metal concentration on the colloid surface and the potential of Th polymer at the colloid surface was estimated. These estimations are important since polymerization may have an increasing effect on the distribution coefficient. The highest distribution

Table 3  
Comparison of  $K_d$  ( $\text{mL g}^{-1}$ ) data from the literature with those calculated using the model developed in this study

Colloid material	Colloid size (nm)	pH	$C_{\text{Th}}$ (M)	Log $K_d$ (Exp)	Log $K_d$ (Mod)	Reference
$\text{Al}_2\text{O}_3$	200	6–7	$5.8 \times 10^{-5}$	4.5	4.5–5.0	Hongxia et al. (2006)
$\text{SiO}_2$	25	3	$2.6 \times 10^{-6}$	1.6	1.8	Östhols (1995)
$\text{SiO}_2$	20?	4–10	$3.2 \times 10^{-5}$	2.75	2.8	Chen and Wang (2007)
$\text{TiO}_2$	30	5–11	$7.2 \times 10^{-6}$	5.0	5.0–5.5	Tan et al. (2007)
$\text{TiO}_2$	44	4–10	$1-50 \times 10^{-9}$	5.0–5.5	5.0–5.5	Jakobsson (1999)

coefficients were achieved in the pH range of 7 to 8. At low metal concentrations the polymerization can not be observed but it could build-up at the colloid surface for higher Th concentration compared to the site concentration depending on the sorption affinity on the polymers.

The size and to a lower extend the colloid concentration play a role in the value of the distribution coefficient. It was calculated that when the colloid particles have smaller sizes the sorption coefficient increases. As the concentration of the colloid particles was increased there was little difference between the distribution coefficients of 0.1 and 1 ppm. But, as the concentration was increased further significant effects were calculated.

In the comparison of the different colloid types  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  displayed the highest distribution coefficients. These were followed by  $\text{FeOOH}$  and finally  $\text{SiO}_2$ . Since the polymerization effect would increase the sorption coefficients while substituting the nature of the colloid surface, the distribution coefficients at higher Th concentrations become similar due to the polymer chains. However, thorium saturation in the solution apparently occurs prior to polymerization. The  $K_d$  values gained from the literature are comparable with those calculated using the applied model.

## References

- Aellen, T.C., Umbricht, O., Goerlich, W., 1993. The analysis of naturally-occurring radionuclides from uranium and thorium decay series in table mineral waters. *Sci. Total Environ.* 130–131, 253–259.
- Alonso, U., Degueldre, C., 2003. Modeling americium sorption onto colloids: effect of redox potential. *Coll. Surf. A* 217, 55–62.
- Baes Jr, C.F., Mesmer, R.E., 1976. *The Hydrolysis of Cations*. Wiley-Interscience, New York.
- Balistieri, L., Brewer, P., Murray, J., 1981. Scavenging residence times of trace metals and surface chemistry of sinking particles in deep ocean. *Deep-Sea Res.* 28A, 101–121.
- Bitea, C., Müller, R., Neck, V., Walter, C., Kim, J.I., 2003. Study of the generation and stability of thorium(IV) colloids by LIBD combined with ultrafiltration. *Coll. Surf. A* 217, 63–70.
- Chase, Z., Anderson, R.F., Fleisher, M.Q., Kubik, P.W., 2002. The influence of particle composition and particle flux on scavenging of Th, Pa and Be in the ocean. *Earth Planet. Sci. Lett.* 204, 215–229.
- Chen, C.L., Wang, X.K., 2007a. Sorption of Th (IV) to silica as a function of pH, humic/fulvic acid, ionic strength, electrolyte type. *Appl. Radiat. Isotopes* 65, 155–163.
- Chen, C.L., Wang, X.K., 2007b. Influence of pH, soil humic/fulvic acid, ionic strength and foreign ions on sorption of thorium(IV) onto  $\gamma\text{-Al}_2\text{O}_3$ . *Appl. Geochem.* 22, 436–445.
- Corbett, D.R., McKee, B., Duncan, D., 2004. An evaluation of mobile mud dynamics in the Mississippi River deltaic region. *Mar. Geol.* 209, 91–112.
- Coppola, L., Roy-Barman, M., Mulsow, S., Povinec, P., Jeandel, C., 2006. Thorium isotopes as tracers of particles dynamics and deep water circulation in the Indian sector of the Southern Ocean (ANTARES IV). *Mar. Chem.* 100, 299–313.
- Degueldre, C., Ulrich, H.J., Silby, H., 1994. Sorption of  $^{241}\text{Am}$  onto montmorillonite, illite and hematite colloids. *Radiochim. Acta* 65, 173–179.
- Degueldre, C., 1995. Retention of redox sensitive elements in aquifers—the case of neptunium. *J. Environ. Radioact.* 29, 75–87.
- Dominik, J., Schuler, Ch., Santschi, P.H., 1989. Residence times of  $^{234}\text{Th}$  and  $^7\text{Be}$  in Lake Geneva. *Earth Planet. Sci. Lett.* 93, 345–358.
- Dosseto, A., Turner, S.P., Douglas, G.B., 2006. Uranium-series isotopes in colloids and suspended sediments: Timescale for sediment production and transport in the Murray–Darling River system. *Earth Planet. Sci. Lett.* 246, 418–431.
- El-Gamal, A., Nasr, S., El-TaHER, A., 2007. Study of the spatial distribution of natural radioactivity in the upper Egypt Nile River sediments. *Radiat. Meas.* 42, 457–465.
- Feng, H., Cochran, J.K., Hirschberg, D.J., 1999.  $^{234}\text{Th}$  and  $^7\text{Be}$  as tracers for the sources of particles to the turbidity maximum of the Hudson River Estuary. *Estuar. Coast. Shelf Sci.* 49, 629–645.
- Hachiya, K., Sasaki, M., Saruta, Y., Mikami, N., Yasumaga, T., 1984. Static and kinetic studies of adsorption–desorption of metal ions on a  $\gamma\text{-Al}_2\text{O}_3$  surface: 1. Static studies on adsorption–desorption. *J. Phys. Chem.* 88, 23–27.
- Hietan, S., 1956. Studies on the hydrolysis of metal ions. 17. The hydrolysis of the uranium (IV) ion,  $\text{U}^{4+}$ . *Acta Chem. Scand.* 10, 1531–1546.
- Holland, H.D., Kulp, J.L., 1954. The mechanism of removal of ionium and radium from the oceans. *Geochim. Cosmochim. Acta* 5, 214–224.
- Hongxia, Z., Zheng, D., Zuyi, T., 2006. Sorption of thorium(IV) ions on gibbsite: Effects of contact time, pH, ionic strength, concentration, phosphate and fulvic acid. *Coll. Surf. A* 278, 46–52.
- Jakobsson, A.-M., 1999. Measurement and modeling of Th sorption onto  $\text{TiO}_2$ . *J. Coll. Interf. Sci.* 220, 367–373.
- James, R., Healy, T.J., 1972. Adsorption of hydrolysable metal ions at the oxide–water interface. *Coll. Interf. Sci.* 40, 42–52.
- Johnson, G.L., Toth, L.M., 1978. Plutonium (IV) and thorium (IV) hydrous polymer chemistry. Report ORNL/TM-6365. Oak Ridge National Laboratory, Tennessee.
- Li, Yuan-Hui, 1981. Ultimate removal mechanisms of elements from the ocean. *Geochim. Cosmochim. Acta* 45, 1659–1664.
- Lieser, K., 1995. Radionuclides in the geosphere: sources, mobility, reactions in natural waters and interactions with solids. *Radiochim. Acta* 70/71, 355–375.
- Lu, N., Reimus, P., Parker, G.R., Conca, J.L., Triay, I.R., 2003. Sorption kinetics and impact of temperature, ionic strength and colloid concentration on the adsorption of plutonium-239 by inorganic colloids. *Radiochim. Acta* 91, 713–720.
- Martínez-Aguirre, A., García-León, M., Ivanovich, M., 1995. U and Th speciation in river sediments. *Sci. Total Environment* 173–174, 203–209.
- McCarthy, J., Degueldre, C., 1993. Colloidal particles in groundwater and their role in the subsurface transport of contaminants. IUPAC series: Environmental Particle, vol. 2, pp. 247–315.
- McKinley, I., Alexander, W.R., 1993. Constraints on the applicability of “in-situ distribution coefficients” values. *J. Environ. Radioact.* 15, 19–34.
- Nagasaki, S., Tanaka, S., Suzuki, A., 1997. Interfacial behavior of actinides with colloids in the geosphere. *J. Nucl. Mater.* 248, 323–327.
- Neck, V., Müller, R., Bouby, M., Altmayer, M., Rothe, J., Denecke, M.A., Kim, J.I., 2002. Solubility of amorphous Th(IV) hydroxide-application of LIBD to determine the solubility product and EXAFS for aqueous speciation. *Radiochim. Acta* 90, 485–494.

- Murphy, R.J., Lenhart, J.J., Honeyman, B.D., 1999. The sorption of thorium (IV) and uranium (VI) to hematite in the presence of natural organic matter. *Coll. Surf. A* 157, 47–62.
- Niven, Sh.E.H., Moore, R.M., 1993. Thorium sorption in seawater suspensions of aluminium oxide particles. *Geochim. Cosmochim. Acta* 57, 2169–2179.
- Östhols, E., 1995. Thorium sorption on amorphous silica. *Geochim. Cosmochim. Acta* 59, 1235–1249.
- Reiller, P., Moulin, V., Casanova, F., Dautel, Ch., 2002. Retention behaviour of humic substances onto mineral surfaces and consequences upon thorium (IV) mobility: case of iron oxides. *Appl. Geochem.* 17, 1551–1562.
- Righetto, L., Bidoglio, G., Azimonti, G., Bellobono, I., 1991. Competitive actinide interaction in colloidal humic acid–mineral oxide systems. *Environ. Sci. Technol.* 25, 1913–1919.
- Roy-Barman, M., Coppola, L., Souhaut, M., 2002. Thorium isotopes in the western Mediterranean Sea: an insight into the marine particle dynamics. *Earth Planet. Sci. Lett.* 196, 161–174.
- Santschi, P.H., Murray, J.M., Baskaran, M., Benitez-Nelson, C.R., Guo, L.D., Hung, C.-C., Lamborg, C., Moran, S.B., Passow, U., Roy-Barman, M., 2006. Thorium speciation in seawater. *Mar. Chem.* 100, 250–268.
- Smith, P., Degueldre, C., 1993. Colloid facilitated transport of radionuclides through fractured media. *J. Contam. Hydrol.* 13, 143–166.
- Stumm, W., 1987. *Aquatic Surface Chemistry: Chemical Processes at the Particle–Water Interface*. Wiley & Sons.
- Tan, X.L., Wang, X.K., Chen, C.L., Sun, A., 2007. Effect of soil humic and fulvic acids, pH and ionic strength on Th(IV) sorption to TiO<sub>2</sub> nanoparticles. *Appl. Radiat. Isotopes* 65, 375–381.
- Trimble, S.M., Baskaran, M., Porcelli, D., 2004. Scavenging of thorium isotopes in the Canada Basin of the Arctic Ocean. *Earth Planet. Sci. Lett.* 222, 915–932.
- Zhang, L., Min, Chen, Weifeng, Yang, Na, Xing, Yanping, Li, Yusheng, Qiu, Yipu, Huang, 2004. Size-fractionated thorium isotopes (<sup>228</sup>Th, <sup>230</sup>Th, <sup>232</sup>Th) in surface waters in the Jiulong River estuary, China. *J. Environ. Radioact.* 78, 199–216.